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Synthesis, structural, and ε-caprolactone polymerization studies of heteroleptic derivatives of aluminum(III)

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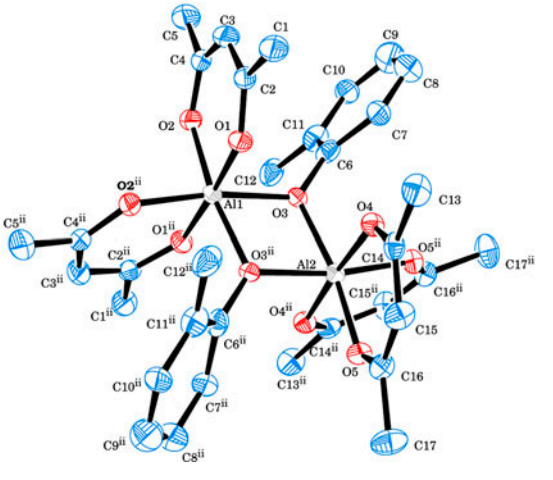

A series of metallo-organic complexes of Al(III), $[(CH_3COCHCOCH_3)_2Al(OR)]_2$ [where R = *o*-MeC_6H_4 (**1**), *m*-MeC_6H_4 (**2**), *p*-MeC_6H_4 (**3**), $C_6H_5CH_2$ (**4**), *o*-$ClC_6H_4CH_2$ (**5**), *m*-$ClC_6H_4CH_2$ (**6**), and *p*-$ClC_6H_4CH_2$ (**7**), were synthesized quantitatively by treating $Al(OPr^i)_3$ with CH_3COCH_2-$COCH_3$ and the phenols (*o*-MeC_6H_4OH, *m*-MeC_6H_4OH, and *p*-MeC_6H_4OH) concerned as well as phenylmethanols ($C_6H_5CH_2OH$, *o*-$ClC_6H_4CH_2OH$, *m*-$ClC_6H_4CH_2OH$, and *p*-$ClC_6H_4CH_2OH$) in suitable stoichiometry using benzene as solvent. All these complexes were soluble in common organic solvents, having sharp melting points, and they were characterized by elemental analysis, IR, and NMR (^1H and ^{13}C) spectral studies. Single-crystal XRD followed by ORTEP diagram of solvated complex (**1a**) revealed its dimeric nature and the existence of six-coordinate aluminum. The complexes were studied in ring-opening polymerization of ε-caprolactone. The molecular weight and polydispersity index values of polycaprolactone were obtained by gel permeation chromatography analysis.

Keywords: Aluminum; Metallo-organic complexes; ε-caprolactone (ε-CL); Ring-opening polymerization (ROP); Polycaprolactone (PCL)

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1. Introduction

Metallo-organic heteroleptic derivatives of aluminum have been of interest due to their low decomposition temperature to obtain nano-structured alumina of high purity and in appreciable yield by sol–gel technology [1]. In addition to this field, analogous complexes have proven their worth in polymerization and biological applications.

Ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) has gained attention due to the excellent biodegradability [2, 3] and biocompatibility of polycaprolactone (PCL). Due to the biocompatible and biodegradable properties, eco-friendly polyesters such as PCL and polylactide as well as their copolymers have been widely used in controlled long-term drug delivery systems [4, 5], biocompatible implants, and in scaffolds for tissue engineering [6, 7]. A variety of aluminum complexes have already been well documented as catalysts for ROP of ε-CL with greater yield, e.g., a series of three-, four-, and five-coordinate aluminum derivatives incorporated with aminophenols [8], pyrazolyl-phenolate ligands [9], salen ligands [10], bis(phenolato)bis(amine) ligands [11], and amine bisphenolate ligands [12, 13].

Some of the main group and transition metal complexes have also been identified as catalysts for ROP to produce polymers with well-controlled structures [14] where the introduction of suitable auxiliary ligands could prevent polymers from trans-esterifications which always occurs as side reactions during the ROP. Aluminum-catalyzed polymerization of cyclic esters has been demonstrated using complexes with the ligands having N and O coordination. This was of interest, mainly due to the success of the complexes bearing salen or salan, imino-phenolate or ketiminate ligands [15, 16]. Some of these exhibit significant advances in stereo-controlled polymerization.

In view of this significant application, in this study, we report seven complexes of β-diketonato derivatives of aluminum(III) which have not been used in ROP of ε-CL without external benzyl alcohol as reported. Further, they are relatively stable and more economical than the complexes documented earlier for polymerizing ε-CL. Though tris (acetylacetonato)aluminum(III) was used in cyclic ester preparation [17], it had no polymerization activity in the absence of external alcohol. Even in the presence of excess alcohol, polymerization proceeded poorly, but our synthetic route gives rapid process without external alcohol.

2. Experimental

2.1. *General*

All reactions were carried out in stringent anhydrous conditions. Solvents and reagents were purified by conventional methods before use [18]. Aluminum triisopropoxide was purchased from Sigma-Aldrich and used as obtained. Cresols and benzyl alcohols were purchased from Avra chemicals and distilled for the experiment. Aluminum and isopropanol were estimated gravimetrically [19] and iodometrically [20], respectively. Melting points were observed on an Elchem digital melting point apparatus. FTIR spectra (4000–400 cm^{-1}) were obtained from a SHIMADZU IR affinity 1 spectrometer with anhydrous KBr pellets. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker ADVANCE III 400 spectrometer in $CDCl_3$ solution at 400 MHz frequency using TMS as an internal standard. The gel

permeation chromatography (GPC) analyses were carried out on a SHIMAZDU-PROMINENCE instrument in THF at room temperature. Molecular weights and molecular weight distributions were calculated using polystyrene as standard. Elemental analyses of complexes were done on an Elementar Vario EL III instrument.

2.2. *Preparation of [(acac)$_2$Al(o-MeC$_6$H$_4$O)]$_2$ (1)*

Tris(isopropoxy)aluminum(III) (3.28 g, 16.1 mmol) in anhydrous benzene was added to another similar benzene solution of acetylacetone (3.22 g, 32.2 mmol). The reaction mixture was refluxed for 30 min, and then previously dissolved *o*-cresol (1.74 g, 16.1 mmol) in benzene was added to the former reaction mixture and refluxing was continued for 4 h. The liberated alcohol was collected as an azeotrope of benzene and isopropanol and the reaction progress was monitored, while estimating it by oxidimetric method. Reaction mixture was concentrated by distilling out pure benzene. At room temperature, fine colorless diffractable quality crystals of **1a** appeared in the flask. The excess solvent was removed under vacuum to furnish white solid **1**. The product was washed twice with *n*-hexane. Yield, 4.86 g, 93%. mp = 172–174 °C. ^{1}H NMR (400 MHz, DMSO d_6, 25 °C): δ (ppm) 1.86 (s, 24 H, CH_3), 2.11 (s, 6 H, CH_3), 5.52 (s, 4 H, C*H*), 6.66–6.70 (t, 2 H, J = 8.0 Hz, Ar–*H*), 6.75–6.77 (d, 2 H, J = 8.0 Hz, Ar–*H*), 6.96–7.00 (t, 2 H, J = 8.0 Hz, Ar–*H*), 7.03–7.05 (d, 2 H, J = 8.0 Hz, Ar–*H*). ^{13}C NMR (100.65 MHz, $CDCl_3$, 25 °C): δ (ppm) 15.89(Ar*C*H$_3$), 26.71 (*C*H$_3$), 101.33(*C*H), 115.11(Ar–*C*), 120.11(Ar–*C*), 124.04(Ar–*C*), 128.36(Ar–*C*), 130.82 (Ar–*C*), 154.33(Ar–*C*), 191.63(*C*O). FTIR (solid KBr) ν = 2964, 2922, 2854, 1598, 1529, 1454, 1402, 1029, 775, 613. Anal. Calcd for $C_{34}H_{42}Al_2O_{10}$: C, 61.4; H, 6.4%. Found: C, 61.5; H, 6.6%.

In view of physical appearance and pattern of reaction, similar synthetic route has been employed for the remaining six (**2–7**) complexes.

2.3. *Preparation of [(acac)$_2$Al(m-MeC$_6$H$_4$O)]$_2$ (2)*

Yield, 3.81 g, 89%. mp = 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 1.91 (s, 24 H, CH_3), 2.21 (s, 6 H, CH_3), 5.41 (s, 4 H, C*H*), 6.58 (bs, 4H $_{\text{(doublet merged with singlet)}}$, Ar–*H*), 6.62–6.64 (d, 2 H, J = 8.0 Hz, Ar–*H*), 6.99–7.03 (t, 2 H, t, J = 8.0 Hz, Ar–*H*). ^{13}C NMR (100.65 MHz, $CDCl_3$, 25 °C): δ (ppm) 20.33(Ar*C*H$_3$), 25.67(*C*H$_3$), 100.28(*C*H), 111.46(Ar–*C*), 115.13(Ar–*C*), 119.96(Ar–*C*), 128.17(Ar–*C*), 138.46(Ar–*C*), 154.96(Ar–*C*), 190.59(*C*O). FTIR (solid KBr) ν = 3034, 2997, 2920, 1600, 1533, 1446, 1382, 1029, 773, 609. Anal. Calcd for $C_{34}H_{42}Al_2O_{10}$: C, 61.4; H, 6.4%. Found: C, 61.2; H, 6.3%.

2.4. *Preparation of [(acac)$_2$Al(p-MeC$_6$H$_4$O)]$_2$ (3)*

Yield, 4.86 g, 91%. mp = 119–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 1.98 (s, 24 H, CH_3), 2.24 (s, 6 H, CH_3), 5.48 (s, 4 H, C*H*), 6.73–6.75 (d, 4 H, J = 8.0 Hz, Ar–*H*), 6.96–6.98 (d, 4 H, J = 8.0 Hz, Ar–*H*). ^{13}C NMR (100.65 MHz, $CDCl_3$, 25 °C): δ (ppm) 20.48(Ar*C*H$_3$), 26.72(*C*H$_3$), 101.31(*C*H), 115.28(Ar–*C*), 129.19(Ar–*C*), 129.87 (Ar–*C*), 153.85(Ar–*C*), 191.63(*C*O). FTIR (solid KBr) ν = 3000, 2922, 1598, 1535, 1402, 1384, 1029, 767, 607. Anal. Calcd for $C_{34}H_{42}Al_2O_{10}$: C, 61.4; H, 6.4%. Found: C, 61.1; H, 6.2%.

2.5. *Preparation of [(acac)$_2$Al(OCH$_2$ C$_6$H$_5$)]$_2$ (4)*

Yield, 4.26 g, 91%. mp = 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 1.99 (s, 24H, CH_3), 4.69 (s, 4H, CH_2), 5.48 (s, 4H, C*H*), 7.26–7.37 (m, 10H (overlapped peaks of aromatic protons), Ar–*H*). ^{13}C NMR (100.65 MHz, $CDCl_3$, 25 °C): δ (ppm) 26.78(*C*H$_3$), 65.36 (*C*H$_2$), 101.15(*C*H), 127.00(Ar–*C*), 127.65(Ar–*C*), 128.57(Ar–*C*), 140.92(Ar–*C*), 191.49 (*C*O). FTIR (solid KBr) ν = 3022, 2922, 2875, 1604, 1531, 1413, 1384, 1026, 736, 640. Anal. Calcd for $C_{34}H_{42}Al_2O_{10}$: C, 61.4; H, 6.4%. Found: C, 61.3; H, 6.3%.

2.6. *Preparation of [(acac)$_2$Al(o-ClC$_6$H$_4$CH$_2$O)]$_2$ (5)*

Yield, 2.61 g, 94%. mp = 195–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 1.92 (s, 24H, CH_3), 4.73 (s, 4H, CH_2), 5.41 (s, 4H, C*H*), 7.15–7.24 (m, 4H (overlapped peaks of aromatic protons), Ar–*H*), 7.28–7.30 (d, 2H, J = 8.0 Hz, Ar–*H*), 7.41–7.42 (d, 2H, J = 4.0 Hz, Ar–*H*). ^{13}C NMR (100.65 MHz, $CDCl_3$, 25 °C): δ (ppm) 26.76(*C*H$_3$), 62.73(*C*H$_2$), 101.14 (*C*H), 127.01(Ar–*C*), 128.67(Ar–*C*), 128.73(Ar–*C*), 129.29(Ar–*C*), 132.63(Ar–*C*), 138.32 (Ar–*C*), 191.49(*C*O). FTIR (solid KBr) ν = 3061, 2922, 2877, 1604, 1529, 1413, 1031, 761, 626. Anal. Calcd for $C_{34}H_{40}Al_2Cl_2O_{10}$: C, 55.7; H, 5.5%. Found: C, 55.4; H, 5.4%.

2.7. *Preparation of [(acac)$_2$Al(m-ClC$_6$H$_4$CH$_2$O)]$_2$ (6)*

Yield, 3.70 g, 92%. mp = 200–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 1.92 (s, 24H, CH_3), 4.61 (s, 4H, CH_2), 5.41 (s, 4H, C*H*), 7.16–7.22 (m, 6H (overlapped peaks of aromatic protons and solvent), Ar–*H*), 7.30 (s, 2H, Ar–*H*). ^{13}C NMR (100.65 MHz, $CDCl_3$, 25 °C): δ (ppm) 25.72(*C*H$_3$), 63.30(*C*H$_2$), 67.86(*C*H$_2$), 100.11(*C*H), 123.85(Ar–*C*), 125.95 (Ar–*C*), 126.57(Ar–*C*), 128.72(Ar–*C*), 128.91(Ar–*C*), 133.33(Ar–*C*), 190.45(*C*O). FTIR (solid KBr) ν = 3059, 2922, 2883, 1602, 1529, 1409, 1382, 1028, 769, 632. Anal. Calcd for $C_{34}H_{40}Al_2Cl_2O_{10}$: C, 55.7; H, 5.5%. Found: C, 55.7; H, 5.6%.

2.8. *Preparation of [(acac)$_2$Al(p-ClC$_6$H$_4$CH$_2$O)]$_2$ (7)*

Yield, 5.01 g, 92%. mp = 207–209 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 1.99 (s, 24H, CH_3), 4.68 (s, 4H, CH_2), 5.48 (s, 4H, C*H*), 7.31–7.32 (m, 8H (overlapped peaks of aromatic protons), Ar–*H*). ^{13}C NMR (100.65 MHz, $CDCl_3$, 25 °C): δ (ppm) 26.77(*C*H$_3$), 64.47 (*C*H$_2$), 101.15(*C*H), 128.27(Ar–*C*), 128.65(Ar–*C*), 139.38(Ar–*C*), 191.49(*C*O). FTIR (solid KBr) ν = 3066, 2920, 2872, 1600, 1529, 1413, 1384, 1028, 815, 657. Anal. Calcd for $C_{34}H_{40}Al_2Cl_2O_{10}$: C, 55.7; H, 5.5%. Found: C, 55.4; H, 5.3%.

2.9. *X-ray crystallography*

Diffractable quality colorless crystals of [(acac)$_2$Al(*o*-MeC$_6$H$_4$O)]$_2$·C$_6$H$_6$ (**1a**) appeared in the mother liquor within a few minutes after completion of the reaction. A Bruker SMART APEX II diffractometer was employed to collect the intensity data for the single crystal of **1a**. By applying the direct phase determination technique, the crystal structure was established and further it was refined by full-matrix least-squares on F^2 using SHLEXL-97 [21]. WinGX suite of programs (version 1.85.05) [22] were used for the entire structural calculations. All non-hydrogen atoms were identified from Fourier maps, while hydrogens have

Table 1. Crystal data and structure refinement summary.

Empirical formula	$C_{34}H_{42}Al_2O_{10}C_6H_6$
Formula weight	742.74
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	$a = 13.772(5)$ Å; $\alpha = 90°$ $b = 24.694(5)$ Å; $\beta = 97.675(5)°$ $c = 11.772(5)$ Å; $\gamma = 90°$
Volume	3968(2) Å^3
Z	4
Density (calculated)	1.243 Mg/m^3
Absorption coefficient	0.128 mm^{-1}
F(0 0 0)	1576
Crystal size	0.2 × 0.27 × 0.3 mm^3
Theta range for data collection	1.649–26.528°
Index ranges	$-17 \le h \le 17$, $-30 \le k \le 30$, $-14 \le l \le 14$
Reflections collected	25,874
Independent reflections	4096 [*R*(int) = 0.0613]
Completeness to $\theta = 25.242°$	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4096/0/236
Goodness of fit on F^2	1.042
Final *R* indices [$I > 2$ sigma(*I*)]	*R*1 = 0.0748, *wR*2 = 0.2291
R indices (all data)	*R*1 = 0.1427, *wR*2 = 0.2879
Extinction coefficient	n/a
Largest diff. peak and hole	0.828 and −0.373 e Å^{-3}

been stereochemically fixed and refined as riding. The concerned crystal data are displayed in table 1.

2.10. *Polymerization of ε-CL*

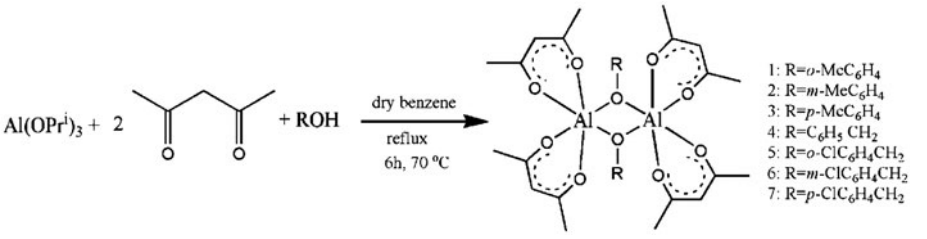
A solution of catalyst (0.2 mmol) in DCM was added to another solution of ε-CL (20.0 mmol) and DCM. The reaction mixture was stirred in an oil bath at 50 °C for the required time. After quenching the polymerization by addition of methanol, the reaction mixture was poured into methanol for precipitation of PCL as a white solid. The obtained polymer was purified by dissolving in DCM and by precipitating it with methanol. The polymer was further dried in a vacuum oven at 50 °C to get a constant weight.

Polymerization did not proceed with **1**, **2,** and **3,** but remaining derivatives of Al(III) exhibited good speed, even without addition of external benzyl alcohol, magnifying the significance of the work.

3. Results and discussion

3.1. *Synthesis and characterization*

Aluminum(III) derivatives (**1–7**) were synthesized via *in situ* alcohol elimination reactions in appreciable yield (scheme 1). Reaction of $Al(OPr^i)_3$ with $CH_3COCH_2COCH_3$ and ROH in 1 : 2 : 1 M ratios in refluxing anhydrous benzene yielded dinuclear complexes $[(CH_3COCHCOCH_3)_2Al(OR)]_2$ as shown below:



Scheme 1. Synthesis of aluminum(III) derivatives (**1–7**) of the type $[(CH_3COCHCOCH_3)_2Al(OR)]_2$.

All these reactions were quite facile and their progress was monitored by estimating the isopropanol liberated as an azeotropic mixture of benzene-isopropanol collected during the course of reaction by iodometric titration. The obtained crude products were purified with anhydrous *n*-hexane. Finally, white solids with sharp melting points, soluble in common solvents such as toluene, dichloromethane, and chloroform appeared.

Newly synthesized derivatives were characterized by FTIR, ^{1}H NMR, ^{13}C NMR, and elemental analyses. Good-quality crystals of **1a** appeared in the reaction mixture, and its structure was determined by single-crystal XRD. XRD of **1a** reveals the presence of entrapped benzene molecule. Afterward, repurification and drying of it as well as other analogs of the series confirmed products free from molecular benzene observed in single-crystal XRD.

In FTIR spectra of the complexes, the disappearance of peaks from 3400 to 3100 cm^{-1} due to free OH of ligands (enolic OH of acetyl acetone and free OH of cresols and benzyl alcohols used) indicated deprotonation of ligands and appearance of peaks in the region 680–607 cm^{-1} indicated formation of Al–O bond. The shifting of the C=O stretching frequency from 1735–1625 to 1602–1598 cm^{-1} and the appearance of a strong band at 1535–1529 cm^{-1} due to C=C indicated bidentate coordination of acetylacetone. A couple of peaks at 3066–2854 cm^{-1} correspond to stretching frequencies of Ar–H and C–H (of CH_3 in cresols and CH_2 in benzyl alcohols). The absorption bands at 1021–1026 cm^{-1} revealed C–O stretching vibrations of bridged alkoxy and aryloxy groups. Peaks at 815–736 cm^{-1} confirmed Al–O–Al vibrations.

From the ^{1}H NMR spectra of **1–7**, the absence of doublets at 1.10–1.40 ppm and multiplet at 4.20–4.50 ppm indicates complete removal of isoporoxy groups. Disappearance of free OH peaks indicated deprotonation of hydroxy groups of acetylacetone, cresols, and benzyl alcohols. In the ^{1}H NMR of all the complexes, one singlet of all methyl and another singlet for methine protons of acetylacetonate moiety appeared at 1.88–1.99 ppm and 5.41–5.52 ppm, respectively. Further, a singlet at 2.11–2.24 ppm was the signature of methyl protons of methylphenolate in **1–3**. A singlet at 4.61–4.73 ppm confirms the existence of every methylene proton of benzyl alcoholate moiety in **4–7**. The ^{1}H and ^{13}C NMR spectra of all these complexes recorded at room temperature revealed identical chemical environment for the following set of protons along with their interpretation: all the methyl protons of acetylacetonate moiety, entire methine protons of the same β-diketonate moiety, every methyl protons of methylphenolate moiety, and both the methylene protons of benzyl alcoholate moiety [23, 24].

The structural analysis was carried out using X-ray crystallography. The monoclinic complex crystallized (**1a**) in the *C2/c* space group, in a centrosymmetric structure (figure 1), generated using symmetry equivalent position at $(2 - x, y, \frac{1}{2} - z)$. From the ORTEP

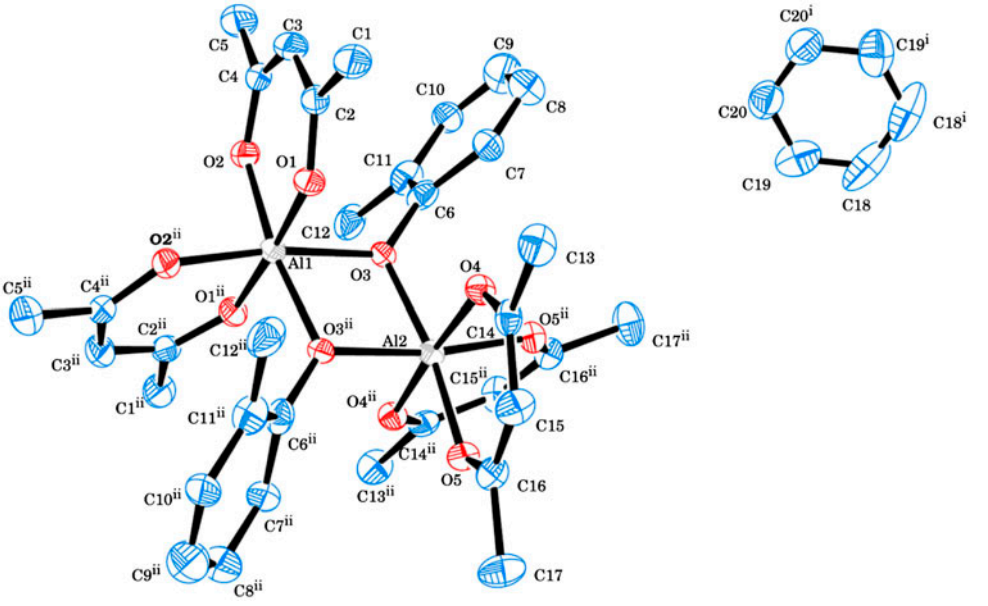


Figure 1. ORTEP plot of **1a**. Hydrogens were omitted for clarity.

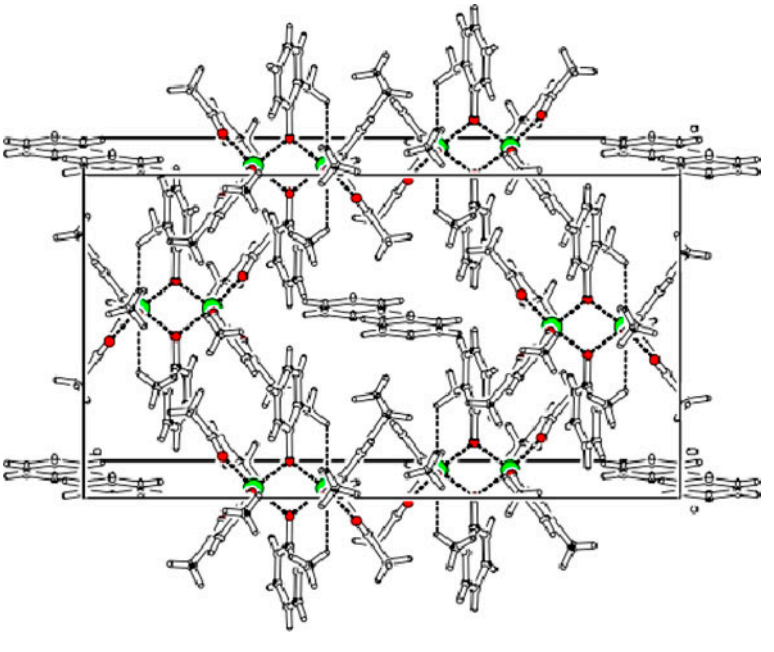


Figure 2. Crystal packing of **1a**.

Table 2. Data of hydrogen bonding in crystal structure of **1a**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	Angle (°)
C(7)–H(7)···O(4)	0.93	2.52	3.198(5)	130
C(12)–H(12C)···O(2)	0.96	2.57	3.297(6)	133
C(12)–H(12C)···O(1)	0.96	2.53	3.212(7)	128

Note: Symmetry equivalent position at: $-x, y, \frac{1}{2} - z$.

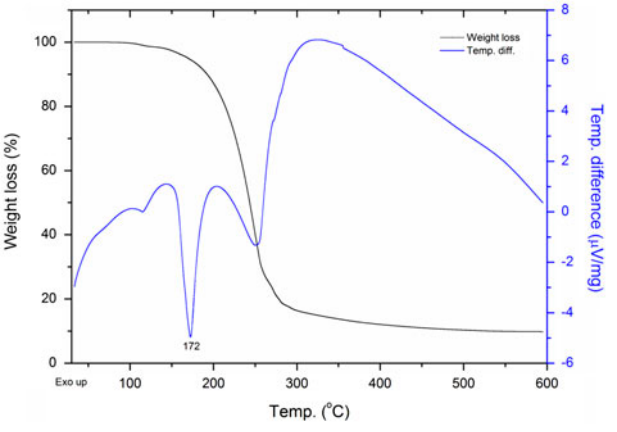


Figure 3. TGA-DSC of **1**.

diagram (figure 1), we infer that the torsion angle values exhibit symmetry equivalence of pentane-2-4-dione units coordinated with aluminum almost perpendicular (86.9° and 88.3°) and that these units oriented by 77.6(1)° are revealed by least-squares plane calculation. The maximum RMS deviation of pentane-2-4-dione mean plane parameter was 0.027(1) Å. The six-coordinate Al–O bridging bond distances were longer than standard, but around aluminum, bond angles are in agreement with previous reports [23, 25]. In the crystal packing and molecular structure (figure 2), analysis of potential hydrogen bonds revealed C–H···π interactions, weak C–H···O hydrogen bonds, and aromatic hydrogen bonds [26]. The contribution of solvent benzene had lesser C–H···π interaction than expected due to larger distance (4.082(8) Å) between donor and acceptor. In addition to the coordination bonds (Al–O), intramolecular hydrogen bonds exist at C14 and C17 with O5, O6, and O7. Table 2 lists the hydrogen bonds in the molecular structure.

TGA-DSC curve of **1** (figure 3) indicates a single-step decomposition with significant weight loss (>87%) from 100 to 400 °C. An endothermic peak at 172 °C indicates melting of the complex. A minor (*ca.* 4%) weight loss before the melting point could be attributed to elimination of traces of solvent molecules (C_6H_6) associated with the Al(III) derivative.

3.2. *Polymerization studies*

A considerable number of alkoxo derivatives of aluminum(III) have been employed in ε-CL polymerization. Therefore, **1–7** were also tested for ε-CL polymerization activity in DCM at 50 °C. Derivatives **1**, **2,** and **3** showed no activity, while **4**, **5**, **6,** and **7** were quite active

Table 3. Polymerization of ε-CL catalyzed by **1**, **4**, **5**, **6,** and **7**.[a]

Entry	Cat.	$[M]_o : [Al]_o : [ROH]_o$	*T* (°C)	Time (h)	Conv.[b] (%)	M_n[c] (calcd)	M_n[d] (obsd)	Yield[e] (%)	PDI[d]
1	**5**	100 : 1 : 0	25	48	15	2300	900	20	1.00
2	**5**	100 : 2 : 0	50	2	95	5600	5400	95	1.18
3	**5**	100 : 1 : 0	50	2	90	10,400	7700	92	1.45
4	**5**	300 : 2 : 0	50	2	90	15,600	9100	93	1.47
5	**5**	200 : 1 : 0	50	4	87	20,000	11,000	89	1.40
6	**5**	100 : 1 : 0	70	2	93	10,800	8000	91	1.55
7	**4**	100 : 1 : 0	50	8	87	10,000	7500	87	1.58
8	**6**	100 : 1 : 0	50	5	91	10,500	8500	93	1.38
9	**7**	100 : 2 : 0	50	3	92	5400	5400	87	1.38
10	**7**	100 : 1 : 0	50	3	95	11,000	10,600	94	1.35

[a]All polymerization reactions were carried out in 15 mL of DCM.
[b]Measured from ^{1}H NMR analysis.
[c]M_n (calcd) = [114.14 × $[M]_o : [Al]_o$ × conversion yield/($[ROH]_{eq}$)] + M(ROH).
[e]Isolated yield.
[d]Obtained from GPC analysis.

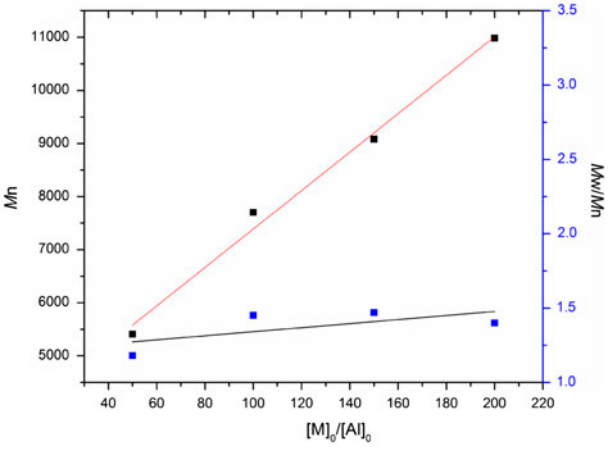


Figure 4. Catalytic polymerization of ε-CL by **5** at 50 °C in DCM.

in polymerizing ε-CL in the absence of external benzyl alcohol. Systematic studies for ε-CL polymerization of **5** were carried out in DCM at different temperatures and for different $[M]_o : [Al]_o$ values (monomer to initiator ratios) under dry nitrogen. The results of catalytic polymerization of ε-CL are shown in table 3. Poor monomer conversion at 25 °C (table 3, entry 1) and good monomer conversion at 50 and 70 °C (table 3, entries 3 and 6) by **5** clearly indicate the temperature dependence of these polymerization reactions. The molecular weight and PDI values of PCL were measured by GPC analysis, and the PDI values were 1.00–1.58, indicating that the polymerizations did not proceed in controlled fashion except in the case of entry 2. The "living" character of ε-CL polymerization by **5** was evidenced by the linear relationship between M_n and $[M]_o : [Al]_o$ at 50 °C (figure 4). From the results of catalytic polymerization, it is evident that **5**, **6,** and **7** (especially **5** and **7**) with chlorine substituted benzyl alcoholato group as the secondary ligand showed good monomer conversion in shorter time than **4** with benzyl alcoholato group as secondary

Figure 5. The ^{1}H NMR spectrum of PCL catalyzed by **5** (entry 2, table 3).

ligand. The enhanced activity of **5**, **6,** and **7** was due to increased Lewis acidity of the aluminum because of electron-withdrawing chlorine on the benzyloxy group which favored binding of monomer to aluminum. Among all the complexes, **5** (table 3, entry 2) was best with a high rate of polymerization within 2 h for 95% conversion, whereas **4** (table 3, entry 7) showed poor catalytic polymerization activity by taking 8 h for attaining 87% conversion. The ^{1}H NMR of PCL ($[M]_o : [Al]_o = 100$; table 3, entry 3), as shown in figure 5, indicates that polymerization took place with a "coordination insertion" pathway. The presence of H_g (CH_2 protons of PCL from hydroxyl group end) at 3.58 ppm and H_b (CH_2 protons of PCL from 2-chlorobenzyloxy group end) at 5.04 ppm with an integral ratio close to 1 demonstrates initiation by insertion of 2-chlorobenzyloxy into ε-CL forming an aluminum alkoxide intermediate, which further reacts with excess lactones giving polyesters [13].

4. Conclusion

On the basis of single-crystal XRD and spectral studies, these complexes are dimeric and both aluminum(III) ions are attached with the ligands in six coordination. These derivatives were tested for ROP of ε-CL. Complexes **1**, **2,** and **3** were almost passive in the absence of

benzyl alcohol, but **4–7** exhibited quite encouraging response during the above said polymerization. Interestingly, **5** revealed the "living" character. Complexes bearing chloro-substituted benzyloxy group as secondary ligand showed a higher rate of polymerization than others, owing to the enhanced Lewis acidic character of aluminum created by electron-withdrawing chlorine of the benzyloxy group.

Supplementary material

With entry number CCDC 1009454, crystallographic data of **1a** have been deposited at the Cambridge Crystallographic Data Center. Copies can be obtained free of charge by requesting to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 (0)1223 336033 or Email: deposit@ccdc.cam.ac.uk).

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Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1042875].

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